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54) Title: NEW METHOD FOR THE SYNTHESIS OF FATTY ACID SUGAR ESTERS

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DETAILED DESCRIPTION OF THE INVENTION

The present invention is concerned with a direct method for the manufacture of sugar esters (SE) from sugar and fatty acid derivatives and is characterized by the use of 2 catalysts with different properties.

In conventional industrial scale production of fatty acid sugar esters with a high degree of substitution, DMF (dimethylformamide) is used as the solvent. There are other patented methods which use dimethylsulfoxide, morpholine or pyridine as the reaction medium.

In Belgian Patent No. 696,700, Osipow reported the new transparent emulsion method (TEm) which uses a nonaqueous, nontoxic medium. A direct synthetic method was introduced in Belgian Patent No. 719,016. In this method, the raw sugar and the fatty acid ester were allowed to react in the presence

of an alkali catalyst at 100-170°C, at 1-15 mm Hg for 3-24 hours. Another type of method was reported in "Chemical Week", September 13, 1969, by the US Department of Agriculture Research Service. In this method, the reaction was carried out in an emulsion of sugar and fats with a metal soap.

In obtaining the derivatives of sugar and fatty acid, the melting point of sugar is quite high and the emulsion materials are unstable at this temperature. Due to these reasons, a direct reaction method has not been possible so far and production of derivatives has been necessary using a solvent medium such as in the DMF method or a special method such as Osipow's TEm.

However, considering the purely chemical reaction without practical aspects, a small amount of sugar ester is produced after a long interaction between the sugar and lower alcohol ester from a high fatty acid in spite of their immiscibility. Naturally, a reaction in which such a small amount is obtained is of no industrial value. Furthermore, in case the SE obtained is only the poly SE, highly substituted with fatty acids, and this gives quite different properties from those widely used SE's where the degree of substitution is less than 2. Therefore, it is generally considered that the solvent methods with completely dissolved sugar or the TEm method are more practical.

Among these methods, the present invention is most closely related to the direct synthesis method reported in the Claim of Belgian Patent No. 719,016. The summary of this patent claim is that SE is obtained using raw sugar by direct reaction at 140-145°C for a long period, namely 3-20 hours.

However, in this method, a long reaction time is unavoidable and the product obtained is only a polyester SE (poly SE), highly substituted with fatty acid groups. This method, claimed in Belgian Patent No. 719,016, can be seen as a simple and economical method, but it has 2 big disadvantages, as described above.

The present invention overcomes these 2 shortcomings and is the simplest method for the manufacture of SE's, which can be applied to production on an industrial level.

Namely, in this invention, a reaction time of 1-3 hours is sufficient and it is possible to produce SE's with a degree of substitution less than 2. The method is comparable to the conventional DMF method or the TEm method.

The present invention represents the creation of a direct reaction procedure, which is characterized by the simultaneous use of catalysts compatible with a small amount of SE, sugar and fatty acid ester, allowing the sugar and fatty acid alkyl ester to interact at a temperature above 140°C.

The technically important points of this invention are the results of extensive research to overcome the shortcomings of the direct reaction method and may be summarized as the following 4 points:

- (1) The size of sugar granules is reduced as much as possible to maximize the surface area. The specific gravity of crystalline or solid sugar is higher than that of a high fatty acid ester by 0.5-0.8 units at 100°C. Therefore, these granules sediment and are separated even when highly efficient stirring is applied. However, when the size of the sugar granules is 100 mesh to 150 mesh, this powdered sugar remains suspended in the methyl ester.

In this reaction, the variation of sugar granule size makes a considerable difference. However, for practical purposes, powdered sugar prepared by a conventional grinder gives satisfactory results.

- (2) The second important point is the utilization of a substance, SE, which gives a medium in which the sugar and the methyl ester are miscible. The effect of using this substance is remarkable and is one of the major aspects of this invention. For this mutually miscible medium, one can use soap and other anionic or nonionic surfactants. Compounds with a high ether bond content, such as PEG, PPG, etc., are also effective to some degree. However, SE is the most preferred compound, since some of the compounds listed above will have to be separated from the product and this is quite difficult to do.

In the case of SE, the use of a moderately substituted SE is preferred to one with a low degree of substitution. In order to obtain the same effect with soap as that with SE, a large quantity of soap is required and the removal of the soap from the product becomes necessary. Therefore, the use of soap is not advantageous. The use of other compounds may also be accompanied by the limitations of being used with SE or requiring separation from the products.

A larger amount of SE is better, but production efficiency decreases. The optimum range is 3-30 weight % relative to the reactants, but 10 weight % is fully effective.

- (3) The third significant factor in the reaction is to increase the efficiency of the catalyst, to increase the rate of the direct reaction and to shorten the reaction time. Extensive study revealed that the simple selection of catalyst and adjustment of its amount do not accomplish the desired improvement. After further research, it was found that a marked increase in catalytic efficiency can be obtained by the combination of two catalysts, chosen from two separate groups with different properties. One of the catalyst groups is easily soluble in one of the reactants, the methyl ester, and the other group of catalysts has a strong compatibility with sugar or melted sugar. The former catalysts include catalysts that are compatible with high fatty acid esters, namely, K, Na or Li alcoholates using methyl, ethyl or propyl alcohols; fatty acid salts of Na, K or Li; and aliphatic amines with high boiling points such as laurylamine.

The catalyst group that has a strong compatibility to sugar as well as to melted sugar is hydrophilic and includes hydroxides, oxides, carbonates or bicarbonates of alkali metals or alkaline earth metals, such as KOH, NaOH, LiOH, K_2CO_3 , $KHCO_3$, Na_2CO_3 and $NaHCO_3$.

Amines may be considered to be compatible with both sugar and methyl ester, but they are very difficult to remove from the products and therefore they are not suitable.

The catalysts are thought to act on sugar chains and simultaneously to serve as a deterrent of the coalescence of melted sugar. This effect may be enhanced by the addition of a finely powdered inorganic alkali.

- (4) The 4th factor for the reaction is the temperature. In a direct reaction, it is very difficult to allow 2 incompatible compounds to interact by any means.

Furthermore, if the reactant is in the crystalline state, or is an aggregate [illegible]. Hence, in an industrial application of a direct reaction method, it is necessary to melt and dissolve the solid reactants, such as sugar, to shorten the reaction time to an industrially feasible range.

Thus, the reaction temperature must be at least the temperature at which the sugar can melt in the reaction system. Pure sugar does not melt until the temperature reaches 180-200°C. However, at this temperature, thermal degradation of the sugar occurs simultaneously with melting. This degradation of the sugar produces caramel with strong coloration and SE may be produced but the conditions are not appropriate for industrial application. The present inventors found that this problem can be overcome by the use of an auxiliary agent for melting the sugar. SE itself is a good auxiliary agent, as already mentioned under (2) and some catalysts compatible with sugar, such as those cited in (3) have the property of acting as auxiliary agents.

In the present invention, the reaction temperature is $155 \pm 10^\circ\text{C}$ and this is the optimum temperature at which sugar begins to soften and melt without degradation due to the auxiliary agent. At the surface of the fine grains of powdered sugar, the sugar molecules are in the state where they can melt easily. Therefore, in the presence of a small amount of auxiliary agent, such as SE, it is thought that the sugar is gradually transformed to the reactive state.

If the reaction temperature is below $155 \pm 10^\circ\text{C}$, the rate of reaction slows down considerably. However, above 165°C , the fine powdered sugar grains adhere to one another and coagulate even in the presence of SE or coagulation inhibitor and separate completely from the methyl ester layer. Thus, the applicable temperature is limited to a relatively narrow range.

The direct reaction method must satisfy these four significant factors or conditions.

Moreover, during the reaction process, by-products formed in ester exchange reactions, such as low-molecular alcohols, appear and it is necessary to keep the reaction system at a low pressure to remove these by-products. A lower pressure is more favorable for increasing the rate of reaction, but 50-100 mm Hg abs is satisfactory. Examination of the reaction process indicates that, at the beginning, fine grains of sugar become suspended in the substrate ester and, as the temperature rises, the surface of these grains gradually begins to soften.

This softened sugar interacts very slowly with the substrate ester to produce SE. This produced SE further interacts with the substrate ester to form SE with a higher degree of substitution and, simultaneously, interacts with the softened sugar to produce SE with a lower degree of substitution. Therefore, once the reaction starts, the rate of reaction increases rapidly and it is believed that the substrate ester interacts with new supplies of sugar molecules, using SE as the medium.

An attempt to use a solvent such as water with the intention of simplifying the direct reaction method provides no advantages over the use of a finely powdered sugar from the beginning, because the sugar recrystallizes into large grains upon the removal of the solvent.

The effect of using the method of the present invention is to elevate the direct method of reacting sugar and fatty acid methyl ester to an industrially practical level. Previously, the direct reaction has been quite difficult to apply in industrial production, but now it is possible using various processes. It is clear that this direct method is superior to the other solvent methods and the effects of the method will be described in detail below.

- (1) The time required to reach the predetermined reaction rate has been shortened considerably.
- (2) It has become possible to obtain SE with a low degree of substitution which was difficult previously, using the direct method.
- (3) Reduction of the required amount of catalyst is achieved and simultaneously the occurrence of undesirable hydrolysis is also decreased.
- (4) The coloration of the product is lessened due to the shortening of the reaction time.

These aspects are effective even at the industrial level and the method of the present invention allows the production of SE with better quality and more economically than with other methods.

Practical and Comparison Examples are given below.

Practical Example 1

An amount of extremely hard beef tallow fatty acid ester, 1.45 kg (5 mL)*), was placed into a 20 L capacity reaction chamber equipped with a spiral-type stirrer and was heated to 100°C with continuous stirring. Then 1.71 kg (5 moles) of finely powdered granulated sugar (150 mesh pass) was introduced and the mixture was stirred and dehydrated. The dehydration was carried out at 100-120°C at 50 mm Hg to 25 mm Hg for 30 minutes, followed by the addition of 170 g of SE (the degree of substitution was 1.7) and 51 g of K_2CO_3 . Then the mixture was

*) This 5 mL is an error in the Japanese and should be 5 moles. - Translator.

heated to 150°C and methanolic KOCH₃ (43 g) (143 g as MeOH solution) was added. The reaction was allowed to proceed at 150 ± 3°C at 5 mm Hg ± 2 mm Hg for 3 hours.

As the reaction progressed, MeOH escaped and was collected in a dry ice trap. The amount of this MeOH was 157 g after 2 hours. At this point, a sample was taken for chemical analysis. The reaction was continued for another hour to complete the process. The obtained product was in the liquid form and had a viscosity of a few hundred cps at 150°C but was a soft paste at 60-70°C. At room temperature, it became a hard solid and could be ground into a powder. The sample collected after 2 hours of reaction also became a solid and could be ground at room temperature. The results of the chemical analysis of these samples were as follows:

(1) Sample collected after two hours of reaction

unreacted Me ester content	6.7%
amount of soap produced	1.9%
unreacted sugar	29.5%
analysis of the SE composition:	
monoester	13 %
diester	28.5%
tri- or polyester	57.5%

(2) Final product

unreacted Me ester content	1.5%
amount of soap produced	3.2%
unreacted sugar	21.6%
analysis of the SE composition:	
monoester	38.0%
diester	37.9%
tri or polyester	24.1%

The SE yield in the final product was 90.5% relative to the substrate fatty acid ester and the degree of substitution of the SE was 1.44.

Practical Example 2

Into a reaction chamber with a capacity of 20 L, 835 g (2.5 moles) of solid beef tallow fatty acid propylene glycol ester were introduced and sugar, 1.71 kg, SE 170 g, MeONa 25 g and K₂CO₃ 51 g were introduced in the same manner as in Practical Example 1. The reaction conditions were also the same as in Practical Example 1.

After a reaction time of 1 hour and 30 minutes, the amount of propylene glycol trapped was 17.5 g. The reaction was continued for another hour and then the reaction mixture was cooled. The properties of the product were similar to those of Practical Example 1, but the viscosity and the solidification temperature were a little higher.

The chemical analysis of the obtained product showed the following: The yield of SE in the final product was 95%; soap produced 3.8%. The SE composition was as follows: monoester 51.6%, diester 32.2% and tri or polyester 16.2%. The degree of substitution of the SE was 1.48.

Practical Example 3

Into a 500 cc capacity reaction flask equipped with a thermometer and a vacuum gauge, 42.4 g of extremely hard beef fatty acid methyl ester and 75 g of finely powdered granulated sugar (150 mesh pass) were introduced. The mixture was dehydrated at 50 mm Hg while raising the temperature to 100-120°C. Then a Tween-type, nonionic surfactant with 23 moles of ethylene oxide added was introduced in an amount of 11.2 g together with 35 g of SE (degree of substitution 2.3). This was followed by adding 1.5 g of each of powdered K_2CO_3 and $KOCH_3$. The reaction was carried out at 150°C \pm 3°C and at a pressure of 50 mm Hg. After about 1 hour and a half of reaction time, the trapped MeOH was about 4.5 g. The reaction was continued for 2 more hours and then stopped.

The results of the chemical analysis of the final product showed the following: The yield of SE in the final product was 93.5%; soap produced 1.7%. The SE composition was as follows: monoester 47.5%; diester 30.3% and triester 22.2%. The degree of SE substitution was 1.56.

Practical Example 4

Into a 500 cc capacity reaction flask, 75 g of powdered sugar (150 mesh pass) and 42.4 g of solid beef tallow fatty acid methyl ester were introduced. This was followed by the addition of 10 g of silica gel powder, 4 g of SE and 1.5 g of each of powdered KOH and NaOMe. The reaction was carried out at 150°C and at a pressure of 125 mm Hg for 3 hours.

Results of the chemical analysis of the product showed the following: The yield of SE in the final product was 97%, soap produced 4.7%. The SE composition was as follows: monoester 42%; diester 30.5%; tri or polyester 28.5%. The degree of substitution of the SE was 1.66.

Practical Example 5

Into a 250 cc reaction flask, 34.2 g of powdered sugar (150 mesh pass) and 28.9 g of extremely hard beef tallow were placed. This was followed with 3.5 g of SE (degree of substitution 1.7) and 5 g of a mixture of tallow fatty acid monoglyceride and diglyceride). The reaction was carried out in the presence of the catalysts KOH and KOMe, each added in an amount of 1.5 g. The reaction temperature was 150°C and the pressure 3 mm Hg. The reaction time was 3 hours. A part of the glycerides evaporated out of the system, but the majority remained. The reaction products consisted of SE, glycerides produced, unreacted glycerides and unreacted sugar.

After 3 hours of reaction, the analysis of the reaction product revealed the following: SE 32.7%, glycerides 29.3%, unreacted sugar 30.7%.

The analytical data showed that the degree of substitution of the glyceride was 1.5 and that a mixture of mono-, di- and triesters was obtained. The degree of substitution of SE was 1.4, the amount of monoester was 52%, that of the diester 30.5% and that of the triester 17.5%.

Comparison Example 1

(In this Example, the sugar and methyl ester were reacted directly without using the method of the present invention.)

A reaction between 75 g of sugar (granulated sugar, as in the commercially available form, average 30 mesh) and 42.4 g of beef tallow solid fatty acid methyl ester was carried out at 150°C at 3 mm Hg in the presence of 14 g of K_2CO_3 as catalyst.

The reaction time, the ratio of bound sugar and unreacted methyl ester were as follows.

<u>reaction time (h)</u>	<u>bound sugar (% relative to the product)</u>	<u>unreacted methyl ester (% relative to the product)</u>	<u>soap produced (% relative to the product)</u>	<u>SE yield (%)</u>
3	2.9	27.9	2.2	13.6
6	5.5	12.9	2.4	---
9	6.8	3.0	2.8	85.5
12	7.3	0	4.1	---
22	10.6	0	5.9	---
25.5	11.1	0	6.8	---

As it can be seen, about 12 hours is required to react the Me ester. Furthermore, the SE produced after 12 hours of reaction averaged 4.5 moles of fatty acid per mole of substituted polyester sugar. The content of Belgian Patent No. 719,016 dealt with the reaction described here.

Thus, it is clear that the method of the present invention is superior.

Comparison Example 2

(Comparison Example without the mutually miscible medium.)

The reaction conditions were identical to Practical Example 1, but without the addition of SE with a degree of substitution of 1.7.

<u>reaction time (h)</u>	<u>bound sugar (% relative to the product)</u>	<u>unreacted methyl ester (% relative to the product)</u>	<u>soap produced (% relative to the product)</u>	<u>SE yield (%)</u>
3	7.9	3.6	2.3	87.0
6	15.1	1.0	3.7	---
9	18.7	0	3.5	93.5

The degree of substitution of the obtained SE was 2.27 (after 9 hours of reaction).

Comparison Example 3

(This Comparison Example deals with a reaction without the combination of catalysts.)

The reaction conditions were identical to those of Practical Example 1, but the catalyst was only 140 g of NaOCH_3 . The results were as follows.

reaction time (h)	bound sugar (% relative to the product)	unreacted methyl ester (% relative to the product)	soap produced (% relative to the product)	SE yield (%)
1	5.7	13.7	1.2	---
2	15.7	7.2	2.3	---
3	29.8	6.5	4.5	84.4

The average degree of substitution of the SE was 2.52 after 3 hours of reaction time.

57) Patent Claim

1. This patent deals with a method for a direct reaction for the production of fatty acid sugar esters from finely powdered sugar and fatty acid esters. This patent is characterized by the soap or fatty acid sugar ester as a medium in which the sugar and the fatty acid ester are mutually miscible and by carrying out the reaction at 145-165°C in the presence of a combination of two types of esterification catalysts, one compatible with the sugar and the other with the fatty acid ester.

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Prepn of fatty acid ester of sugar - giving a low degree of substitution in short reaction time using lower temp than previous prepn		
<p>Sugar fatty esters are produced by reacting finely divided sugar with fatty acid ester at 145 to 165°C in the presence of sugar ester and a combination of two types of esterification catalyst, one being compatible with sugar and the other with fatty acid ester.</p>		
<p>ADVANTAGES</p> <p>The sugar ester as the additive, used at 3 to 30% by weight, increases the compatibility of sugar with fatty acid ester and, in conjunction with the specified catalyst system, lowers the fusing temperature of the mix. The combined use of ester-compatible catalysts (lower alcoholate or fatty acid salt of alkali metals, higher alkyl amines, etc.) and sugar-compatible catalysts (hydroxide, oxide, carbonate, bicarbonate of alkali or alkaline-earth metals, etc) effectively accelerates the esterification reaction. The method gives sugar ester of relatively lower degree of substitution, in shorter reaction time and at lower temperature. (6 pp.).</p>		